AD-A062 054 PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY F/G 7/3
PROPERTIES OF REACTIVE ATOMIC SPECIES GENERATED AT HIGH TEMPERA--ETC(U)
1978 P S SKELL AFOSR-75-2748

UNCLASSIFIED AFOSR-TR-78-1497 NL

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COMPLETED PROJECT SUMMARY

CONTRACT/GRANT NO. AFOSR 75-2748

1. TITLE

REACTIVE ATOMIC SPECIES GENERATED AT HIGH TEMPERATURES AND THEIR LOW TEMPERATURE REACTIONS TO FORM NOVEL SUBSTANCES

2. PRINCIPAL INVESTIGATOR -

Dr. Philip S. Skell

3. INCLUSIVE DATES -

10-1-74/5-31-78

4. CONTRACT/GRANT NO. -

AFOSR 75-2748

5. COSTS AND FY SOURCE -

6. SENIOR RESEARCH PERSONNEL (Ph.D. Level)

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Slanga, Joseph
Wilburn, Bruce

8. PUBLICATIONS -

"Reactions of Tungsten and Molybdenum Atoms with 1,3-Butadiene. Tris-(butadiene) tungsten and -molybdenum", with E. M. VanDam and M. P. Silvon, JACS 96, 626 (1974).

"Reactions of Molybdenum and Tungsten Atoms. Syntheses of Bisarene Sandwich Compounds", with M. P. Silvon and E. M. VanDam, JACS 96, (1974).

"Succinimidyl Radical as a Chain Carrier. Mechanism of Allylic Brmination", with J. C. Day, M. J. Lindstrom, JACS 96, 5616 (1974).

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"Succinimidyl and Related Radicals", with J. C. Day, in Organic Free Radicals, ed. by William A. Pryor, (Washington, D.C.: Amer. Chem. Soc., 1978).

"Excited State Succinimidyl in Radical Chain Reactions", with J. C. Day, JACS 100, 1951 (1978).

"Addition Reactions of Imidyl Radicals with Olefins and Arenes", with J. C. Day, M. G. Katsaros, W. D. Kocher, A. E. Scott, JACS 100, 1950 (1978).

"Ground State and Excited State Chemistry of Succinimidyl Radical and its Congeners", with J. C. Day, will appear Accts. Chem. Research.

"Triple Decker Sandwich Compounds: Paramagnetic Triscyclooctatetraenedititanium and its Dianion", with S. P. Kolesnikov and J. E. Dobson, JACS 100, 999 (1978).

COMPLETED PROJECT SUMMARY

CONTRACT/GRANT NO. AFOSR 75-2748

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS -

The major thrust of this program is in the direction of exploration of new methods for vaporizing and studying the reactions of the high boiling elements, during this period for the main part the high boiling transition elements.

We have been successful in carrying out thermal vaporizations of tungsten, molybdenum, rhodium, ruthenium, titanium, zirconium, and thorium. Each of these metals shows an interesting and new chemistry.

Molybdenum and tungsten make a great variety of substituted bis-arene metal compounds. Similar species are produced with benzene when one uses titanium, zirconium, or thorium. These latter compounds are less stable and are generally used as reactants in further transformations. For example, from titanium atoms and benzene or toluene one makes a bis-arene compound which reacts rapidly with cyclooctatetraene to make either the bis-cyclooctatetraene titanium or the tris-cyclooctatetraene bis-titanium. The latter compound was particularly interesting since it turned out to be paramagnetic and it was readily reduced to a diamagnetic material which we postulate to be the triple decker sandwich in which all three cyclooctatetraene rings are planer.

Bis-arene molybdenum and tungsten compounds have been prepared with halogen, methoxyl, carbethoxyl, and dimethylamino substituents. This work was done to prepare not only the homo-complexes, but also the hetero-complexes, in preparation for an examination of the physical properties and chemical properties of these mixed arenes to learn whether or not electronic effects are strongly transmitted between the two halves of the sandwich. That work is now in progress.

The electron transfer properties of metal atoms were examined in their interactions with water and acetone. This led to a new reactivity series, significantly different from the standard potentials for the metals. This is a natural consequence of the very substantial differences in heats of vaporization of the metals. This is interestingly illustrated by the finding that copper and zinc have the same potential as atoms, and that the well known difference in reactivity of the metals must then be due to the large difference in heats of vaporization rather than electronic effects. This atom potential series developed for reactions with

water proved to be the same for reduction of acetone and leads us to suspect that it will be the same for all electron transfer reactions of the metal atoms.

Along lines similar to the acetone work described above was the reaction of magnesium with CO_2, which apparently produces two radical ions, CO_2^-. These radicals can be trapped with olefins to affect the bis-carboxylation of the unsaturated linkage, a reaction hitherto unknown.

The bis-arenes of iron, cobalt, and nickel are not stable at room temperature but prove to be exceedingly interesting zero valent compounds of these metals which with a great variety of ligands will give up the metal atom, liberating the arene. These will prove to be important synthetic intermediates for these elements.

The reaction of nickel atoms with butadiene is important and complex. We have made significant progress in understanding what occurs in this system by identifying a 1:1 nickel-butadiene complex which is stable below -45^{o}. Above that temperature this complex reacts with excess butadiene to make the well known nickel-butadiene trimer. If butadiene is not available to this complex it undergoes a polymerization to make a toluene soluble polymer which still has the same composition of one nickel atom per C4 unit. This is an exceedingly interesting finding and suggests that we may have prepared a hydrocarbon chain with nickel clusters distributed along the chain. Further work with this material continues.

A highly significant finding was made in the field of heterogeneous catalysis. We believe we have prepared a heterogeneous catalyst which has single rhodium atoms as the active sites. This is a rational preparation from which one can easily draw the implication that it would be possible to do the same with all the other metals, and to extend this preparative procedure to the formation of heterogeneous catalysts in which the active sites would be di-atoms, both homo and hetero combinations, or tri-atoms in which the active sites could all be the same atoms or almost any combination of atoms. If this speculation proves to be correct, then the field of heterogeneous catalysis will have available for the first time materials in which the active sites would have a clearly defined molecular composition. This should have highly interesting implications for the mechanisms of heterogeneous reactions, but far more important is the expectation that these

catalysts will have properties significantly different from the usual supported metal catalysts which in essence have particles of metal distributed on the support. The possibility that an important contribution to the preparation of new electrode materials is a clear consequence along these lines. This work makes up an important line of future investigation.

In an area unrelated to metal atom chemistry we have gained strong evidence that succinimidyl radical has been prepared as a reaction intermediate, and that its properties are quite unusual for free radicals. Further we have made the intriguing discovery that it is possible in thermal chain reactions to generate both the ground state and the excited state of this radical, which naturally show quite different reactivities. This idea is being extended to a number of analogous systems.

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: AFOSR-TR-78-1497	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): PROPERTIES OF REACTIVE ATOMIC SPECIES GENERATED AT HIGH TEMPERATURES AND THEIR LOW TEMPERATURE REACTIONS TO FORM NOVEL SUBSTANCES	5. TYPE OF REPORT & PERIOD COVERED: FINAL 10/1/74 5/31/78
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): P. S. SKELL (10) Philip S. Skell	8. CONTRACT OR GRANT NUMBER(s): (15) AFOSR-75-2748
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, The Pennsylvania State University, University Park, PA 16802	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: (16) 61102F 2303/B2 (17) B2
11. CONTROLLING OFFICE NAME AND ADDRESS: AF Office of Scientific Research (NC), Bolling Air Force Base, Bldg. 410, Washington, D.C. 20332	12. REPORT DATE: (11) 1978
	13. NUMBER OF PAGES: 5
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (9) Final rept. 1 Oct 74-31 May 78	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report): Approved for public release; distribution unlimited (12) 6p.	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	
18. SUPPLEMENTARY NOTES	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number): atomic species; chemical elements; reactions; organometallic compounds	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number): A 44 mo. program of research is described which involved the generation of atomic species of a number of chemical elements and their reactions with organic compounds to form organometallic compounds.	

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S/N 0102-014-6601

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